

The Study of Liquid Phase Adsorption on Nanostructured Sorbents in Oil Disperse Systems

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Abstract

Kinetic characteristics of sorbents synthesized from gypsum were studied in a wide range of particle sizes from 15 nm to 1.5 mm. The resulting sorbents based on calcium silicates are chemically and physically stable up to temperatures of 900 - 1,000 K, and represent a suitable material to produce carriers for a wide range of substances. Plate sorbents with a thickness of 1.5 mm were formed from them by sintering. Kinetics of adsorption of each part of oil disperse system was studied. By using the method of immersing the plates in a model oil disperse system, dispersed phase was selectively adsorbed on each plate. The residue of non-adsorbed part of oil disperse system in the experiments did not exceed 2% by mass. The results are useful for modeling oil disperse system in general and in practice for improvement of technological processes of obtaining target products from oil, as well as in the development of disposal and recycling technologies for wastes of production of target products from oil disperse systems.

Keywords: Benzene, Cyclohexane, Hexane, Liquid Phase Adsorption, Oil Disperse Systems

1. Introduction

A disperse medium is a mixture of polar and non-polar compounds that interact with super molecular structures, resulting in formation of solvation shells around super molecular structure. Such a dispersed particle with a complex structure is capable of independent existence and was named a complex structural unit¹.

Oil disperse systems where the disperse phase consists of asphaltene-tarry substances are firstly polydisperse, and secondly high molecular compounds of oil containing up to 88% of carbon and 10% of hydrogen. Asphaltene-tarry substances are concentrated in the heavy oil residues - tar and bitumen. Depending on the depth of selection of distillate fractions and the nature of oil, tar natural resin-asphaltene substances make from 40 to 70% of the heavy oil residue.

Young oil is most rich in tars and asphaltenes (oil of Kazakhstan, Central Asia, Russia) of naphthene-aromatic

or aromatic base, especially tarry. Older paraffinic oil of methane base, as a rule, contains substantially less tars (from tenths to 4%).

Oil disperse systems mainly form colloidal solutions with spherical particles. The bulk consists of particles with a diameter of 2.2 - 3.8 nm, which are formed by association of three to five polyaromatic molecules and are held together by hydrogen and Van der Waals forces. Larger particles with a diameter of 8 - 10 nm form by means of association of main aggregates. These particles can form larger aggregates with a diameter of 22 nm. In individual objects, particles with a size of 300 - 400 nm were found by electron microscopy.

Therefore, studying adsorption of organic substances from oil disperse systems, it is reasonable to use nanostructured sorbents to selectively select particles within the range of nano-sizes.

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2. Justification and Selection of the Object of Research

The structural units of oil disperse system (initial super-molecular structures, their intermediate and final types) have a complex structure due to the nature and geometrical shape of macromolecules of high-molecular compounds, surface forces acting between them, interaction of the disperse phase with the disperse medium and other factors¹.

A characteristic feature of the complex structural unit is the difference of the surface energies between super-molecular structure and the solvent layer and between the solvent layer and the disperse medium. Therefore, complex structural units can interact with the disperse medium. And an urgent task is to study this interaction by using nanostructured sorbents.

Complex structural units of oil disperse system can form free disperse systems (sols) and linked disperse systems (gels).

In a free disperse system, particles of the disperse phase are not linked to each other and can move under external forces (such as gravity).

The disperse phase of linked disperse systems forms a solid frame (spatial structure) in the space, containing the disperse medium.

Oil disperse systems (free or linked disperse systems) are characterized by structural and mechanical strength, i.e., the capability to resist external forces and effects. The greater the force of interaction of macromolecules of high-molecular compounds in the associate and between the associates in the system, the greater the structural and mechanical strength of oil disperse system.

Structural and mechanical strength of oil disperse systems is mainly determined by the thickness of the solvation shell around the supermolecular structure. Such shells have a certain elasticity and cause disjoining pressure, which effects on the particles of oil disperse system and strives to push them apart.

The smaller the thickness of the solvation shell, the higher the structural and mechanical strength of oil disperse system.

The systems studied are arranged in a row by the magnitude of the structural and mechanical strength of the structural unit of oil disperse system: gel, sol, complex structural unit.

The magnitude of the temperature has a significant impact on the structural and mechanical strength of the disperse system. With the temperature increase, the

structural and mechanical strength of the system reduces, tending to zero; at a certain temperature the system goes into a state of a molecular solution.

Thus, the magnitude of the temperature effects on stability of the disperse system.

Kinetic stability of oil disperse system is the capability of a disperse phase to maintain even distribution of a complex structural unit in the disperse medium over a certain time.

Instability of systems has a significant impact on the conduct of the target processes (production, transportation, storage), and requires the development and adoption of appropriate technical measures to protect from lamination¹.

Instability manifests itself in the form of coarsening of the particles of the disperse phase under intermolecular interaction. At the same time, kinetic stability is lost and phase separation occurs, i.e., coagulation. Phase interface decreases. The associates coarsen and precipitate.

To understand the whole mechanism of behavior of oil disperse systems in the target processes (production, transportation, storage), we need to build physical and chemical models of these systems, taking into account nanoscale of their constituent elements.

To this end, consider an oil disperse system as a whole - it is a mixture of about a thousand different substances, of which approximately 80% are liquid hydrocarbons. The portion of sulfur compounds in oil accounts for about 3%, slightly less than oxygen and nitrogen compounds. Oil may contain up to 10% of water and up to 4% of dissolved hydrocarbon gases. Oil composition includes some metal containing substances with nickel and vanadium, mineral salts, solutions of salts of various organic acids and various mechanical impurities.

In various types of oil, the main constituent elements are carbon, hydrogen and sulfur, rarer - oxygen and nitrogen. A particular type of oil can be represented by up to 80 different chemical elements. The carbon content may vary from 82 to 87%, hydrogen - from 11 to 14%, sulfur - from 0.01 to 8%. Oil density varies from 0.7 to 1 g/cm³.

Based on the foregoing, it is reasonable to conduct case studies of oil disperse systems on model mixtures consisting of pre-defined and well studied liquid hydrocarbons.

In this work, we have selected three-component mixture containing hexane, benzene, cyclohexane at a weight ratio of 5:1:1, consisting of substances with similar physical and chemical properties, but reflecting the main features of oil disperse system:

Hexane(C_6H_{14}) - colorless liquid, molecular weight - 86,18 amu, melting point - 95,34 °C, density at [...] - 0,66 g/cm³, boiling point - 68,742 °C.

Benzene (C_6H_6) - colorless liquid with a peculiar pungent smell, aromatic hydrocarbon, melting point - 5,5 °C, boiling point - 80,1 °C, density at 20 °C - 0,88 g/cm³, molecular weight - 78,11 amu.

Cyclohexane (C_6H_{12}) - colorless, thin liquid with a faint smell of camphor, cyclic hydrocarbon, molecular weight - 84.16 amu, melting point - 6,5 °C, boiling point - 81 °C, density at 20 °C - 0,78 g/cm³.

3. Methodical Studies

To study the selected oil disperse system, we used sorbents based on nanostructured calcium silicates, the technology of production is shown in Figure 1.

According to this technology²⁻⁵, at the first step, three phases of aqueous solutions were prepared - gypsum, calcium chloride, and quaternary ammonium salts. Then these solutions were mixed in a ratio of 1:1:1, and subjected to hydrothermal synthesis at a temperature of 800 °C for 8- 10 hours. As a result, a slurry formed to separate the residue with a humidity of 65-75%. The residue was washed with distilled water, combined with anhydrous ethanol and transferred it to drying and crystallization. Five fractions of calcium silicate powder were separated from the target product with a size of (A) 5-10 nm, (B) 15-50 nm, (C) 60-100 nm, (D) 150-250 nm and (E) 300-500 nm. Each of these fractions of calcium silicate powder was pressed and plate adsorbing materials were formed from them by sintering with a thickness of 1.5 mm and an area of 5 cm², with particle sizes (A), (B), (C), (D) and (E) respectively. The resulting samples were calcined at a temperature of 600-750 K and thereby obtained the samples of sorbents with different porosity - (A_1), (B_1), (C_1), (D_1) and (E_1). Figure 1 along with the technology shows surfaces of sorbents with various porosity obtained by means of scanning electron microscope (SEM): a) 0,02-0,029 m³/g (A_1), b) - 0,01-0,02 m³/g (B_1), c) - 0,005-0,01 (C_1) m³/g.

4. Determination of Kinetic Parameters

In the study of physical and chemical properties of sorbents based on calcium silicates (A_1), (B_1), (C_1), (D_1) and

(E_1), it was found that in the air during heating, until the temperature level of 900 - 1000 K, they do not melt and do not change their shape and porosity.

By using the method of immersing plates (A_1), (B_1), (C_1), (D_1) and (E_1) in a certain sequence in oil disperse system, a part of disperse phase was selectively adsorbed onto each plate.

The residue of non-adsorbed part of oil disperse system did not exceed 2% by weight in the experiments.

The study of physical and chemical characteristics of each separated part of oil disperse system showed that with increasing temperature of oil disperse system, the amount of non-adsorbed part (on the sorbent with a maximum porosity value of 0.1-0.5 m³/g (E_1)) decreases to almost zero with increasing temperature from 20 to 50 °C. In this case, the mass of fractions on all sorbent plates was practically unchanged with increasing time of sorption, starting from 100- 120 minute of the experiment.

Table 1 shows the results of the studies of calcium silicate particle size in the sorbent (E_1) with porosity value of 0, 1-0, 5 m³/g.

With increasing porosity of sorbents from 0,005 - 0, 01 m³/g to 0,1 to 0,5 m³/g, the share of semi-volatile fractions on sorbent - highly viscous tar substances, increases. Their amount is growing on all sorbents with increasing temperature of the original oil disperse system.

To conduct the above experimental studies, we used a methodology⁶⁻⁹, which was in the fact that the original liquid organic substance (or a mixture of organic substances) by using a peristaltic pump was transferred to a sorption vessel, where plate nanostructured sorbents with different porosity were placed (A_1), (B_1), (C_1), (D_1) and (E_1). After adsorption, the liquid from the sorption vessel was returned to the original vessel through a reverse loop. Through a parallel loop, the liquid was fed into the flow cell inside ИЭ-5400 B spectrophotometer. The concentration of the solution was measured using a standard spectrophotometric analysis based on the calibration curve at a wavelength of 580 nm. To convert the experimental values of the optical density of solutions into the values of adsorption capacity, extrapolation functions were used based on the experimental data in Freundlich coordinates ($\lg x/m - \lg C$, where x is the amount of adsorbed substance, m is the mass of adsorbent, C is a molar concentration of the substance in solution after adsorption equilibrium is reached). By weighing the mass of the liquid before and after adsorption, the mass of the adsorbed substance was determined. By weighing the plate of

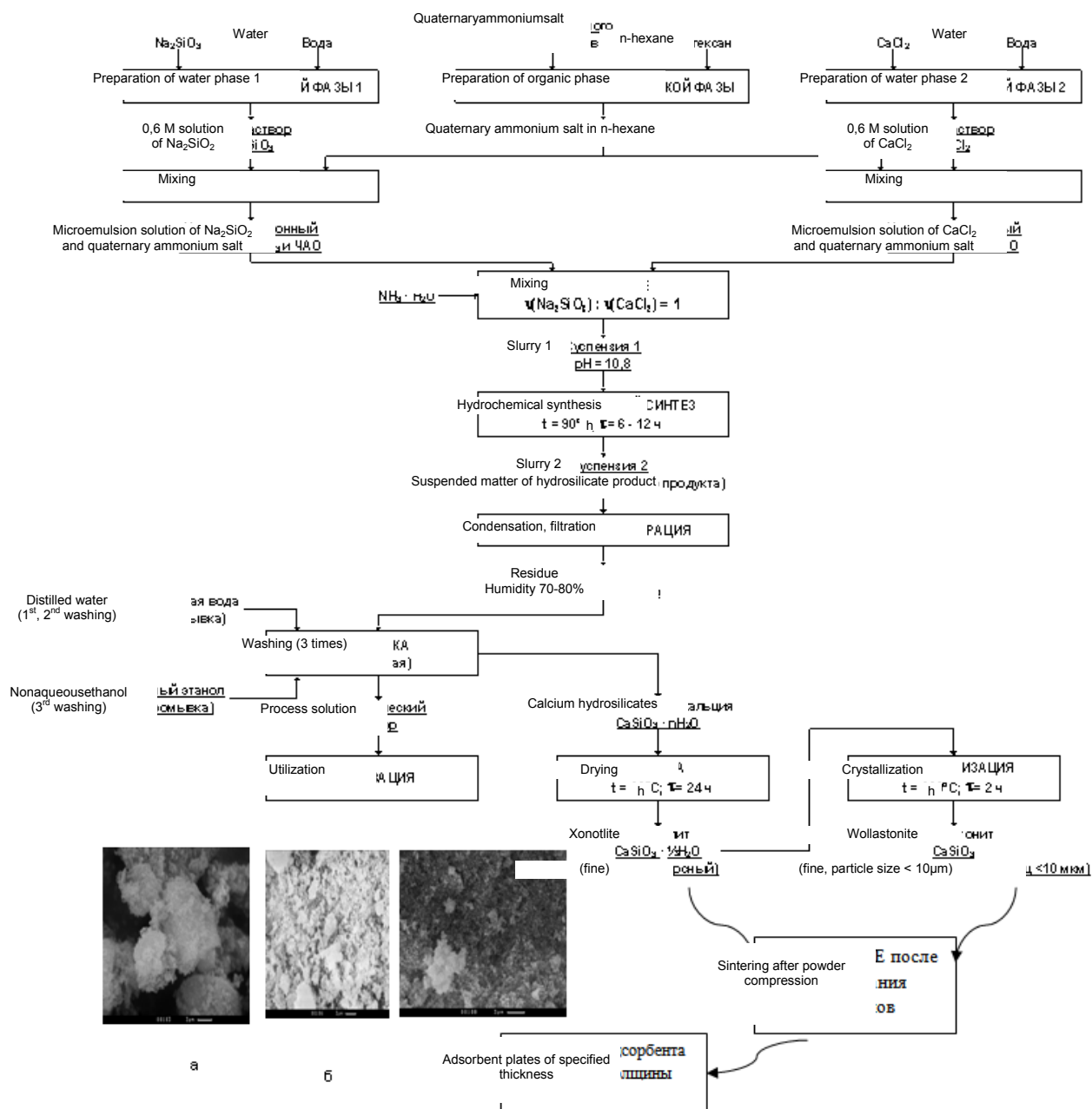


Figure 1. Process flow diagram of making plate adsorbents based on calcium silicates: SEM images of the surface of plate sorbents derived from calcium hydrosilicate powders by standard synthesis (a), with addition of PVA (b), by microemulsion method with quaternary ammonium salt (c).

nanostructured sorbent before and after absorption, the mass of the adsorbed substance was also determined, and previous measurements were controlled. These measurements were made over time, highly accurately measuring the adsorbent capacity for each substance and characteristic time of adsorption.

Thus, nanostructured plate adsorbent with a pre-determined porosity that reaches its capacity the most quickly was determined for each substance (hexane, benzene, cyclohexane). The adsorption was consistently controlled for each nanostructured plate adsorbent by comparing the mass of adsorbed substance with

Table 1. The studies of calcium silicate particle size in the sorbent (E_1) with porosity value of 0,1-0,5 m³/g

Calcium silicates	Particle size and its content (% wt.) in the target product				
	synthesis in the absence of quaternary ammonium salts	Synthesis in changing consumption of methyltriocetylammmonium chloride, %.(wt.)			
		0,05	1,00	2,50	10,00
Xonotlite $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$	21-12 μm 6,4%; 12-3 μm 89,2%; 3-0 μm 4,4%.	21-12 μm 1,3%; 12-5 μm 19,2%; 5-0 μm 79,5 %	21-12 μm 1,4%; 12-5 μm 9,2%; 5-0 μm 89,4 %	21-12 μm 1,3%; 12-5 μm 12,7%; 5-0 μm 86,0 %	21-12 μm 1,8%; 12-5 μm 11,8%; 5-0 μm 86,4 %
Wollastonite CaSiO_3	30-21 μm 2,2%; 21-12 μm 15,3 %; 12-3 μm 73,5 %; 3-0 μm 9 %.	30-21 μm 0,9 %; 21-12 μm 9,7%; 12-5 μm 43,5 %; 5-0 μm 45,9 %.	30-21 μm 0,2 %; 21-12 μm 5,3 %; 12-5 μm 23,5 %; 5-0 μm 71,0 %.	30-21 μm 0,2 %; 21-12 μm 7,3 %; 12-5 μm 27,5 %; 5-0 μm 65,0 %.	30-21 μm 0,7 %; 21-12 μm 6,9 %; 12-5 μm 33,5 %; 5-0 μm 58,9 %.

reference mass for each substance (hexane, benzene, cyclohexane).

4. Conclusions

The experiments conducted allow suggesting that, depending on its porosity, nanostructured plate adsorbents have selective capability in relation to the selected organic compounds. Thus, the longer the molecule of organic compound, the more effective the adsorbent with lower porosity.

When mixing hexane, benzene, cyclohexane in the studied proportion in oil disperse system, there is virtually no their physical and chemical interaction, and with the absorbent they are extracted from the disperse system substantially unchanged.

The results are useful for modeling oil disperse system in general and in practice for improvement of technological processes of obtaining target products from oil, as well as in the development of disposal and recycling technologies for wastes of production of target products from oil disperse systems.

5. References

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